X-ray absorption fine structure spectroscopy of Zr and Hf in HCl solution for chemical characterization of Rf

H. Haba[1], K. Akiyama[2], K. Tsukada[2], M. Asai[2], A. Toyoshima[2], T. Yaita[2], M. Hirata[2], K. Sueki[3], Y. Nagame[2]

[1] RIKEN, Japan
[2] Japan Atomic Energy Research Institute, Japan
[3] Tsukuba University, Japan

haba@riken.go.jp

Introduction

Chemical behavior of the first transactinide element, rutherfordium (Rf), in hydrochloric acid solutions has been investigated by ion-exchange and solvent extraction methods together with the group-4 homologues Zr and Hf [1–5]. On the other hand, relativistic molecular density-functional calculations of electronic structure have been performed for hydrated, hydrolyzed, and chloride complexes of Rf, Zr, and Hf [6]. Although chloride complexation and hydrolysis of Rf have been considered in Refs. [1–6], no structural data of Zr and Hf in HCl solutions, which are essential to discuss the experimental results and to perform the theoretical calculations, are available. The Extended X-ray Absorption Fine Structure (EXAFS) measurements can provide information on the local environment around the central atom such as the atomic number and the number of neighboring atoms and their distance from the central atom. In the present work, we have measured EXAFS spectra of Zr complexes systematically in 1.0–11.5 M HCl. A change in the complex structure with HCl concentration is discussed together with our anion-exchange result of Zr [5].

Experimental procedures

Commercially available $ZrCl_4$ powder was dissolved with 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl solutions to obtain 0.01 M concentration of Zr. EXAFS spectra were collected on the BL27B beam line using a Si (111) monochromater at the High Energy Accelerator Research Organization Photon Factory (KEK-PF). Measurements were performed in the fluorescence mode using a 7-element Ge detector at the Zr *K* edge. Curve-fitting amplitudes and phases were calculated by the FEFF8 code [7].

Results and discussion

Fourier transformed *K*-edge EXAFS spectra of the Zr complexes in 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl solutions, which represent radial distribution functions of the atoms surrounding the Zr atom, are shown by solid curves in Fig. 1 together with the simulations by the FEFF8 code [7] by dotted curves. The FT peaks for shells Zr=O, Zr-O, Zr-Cl, and Zr---Zr are indicated by vertical dashed lines. The structural parameters, the number of neighboring atoms (*N*) and the distance to the neighboring atom (*R*) for shells Zr-O, Zr-Cl, Zr=O, Zr---Zr, and Zr---O, are summarized in Table 1. Accuracy of the *R* and *N* values was estimated to be about ◎}0.02 Å and ◎}0.5, respectively. Note that the spectra shown in Fig. 1 are not corrected for the EXAFS phase shifts, $f¢$, so that each FT peak position does not correspond to the real distance *R* in Table 1.

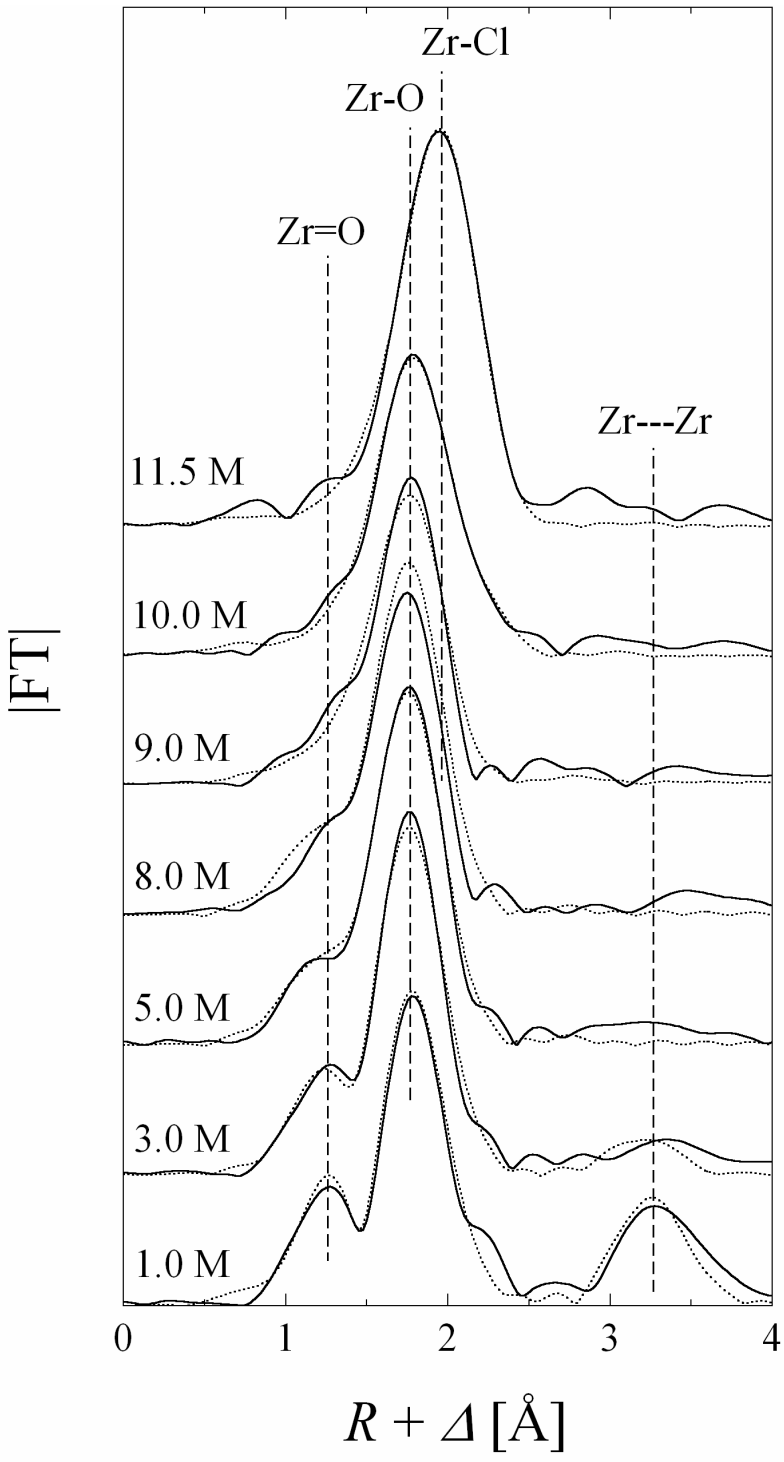

Figure 1. Fourier transformed *K*-edge EXAFS spectra of the Zr complexes in 1.0, 3.0, 5.0, 8.0, 9.0, 10.0, and 11.5 M HCl (solid curves) and the simulations by the FEFF8 code [7] (dotted curves).

Table 1. Structural parameters, the number of neighboring atoms (*N*) and the distance to the neighboring atom (*R*).

[HCl]	Zr-O		Zr-Cl		Zr=O		Zr---Zr		Zr---O	
(M)	*N*	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)	*N*	*R* (Å)
1.0	6	2.21	-	-	1	1.63	1	3.58	4	4.95
3.0	6	2.20	-	-	0.5	1.63	0.5	3.58	-	-
5.0	6	2.21	-	-	0.8	1.65	-	-	-	-
8.0	6	2.22	-	-	-	-	-	-	-	-
9.0	7	2.23	-	-	-	-	-	-	-	-
10.0	4	2.21	3	2.43	-	-	-	-	-	-
11.5	-	-	6	2.43	-	-	-	-	-	-

In Fig. 1, the intense Zr-O peaks for Zr-OH_2 and/or Zr-OH^- bonds are seen at HCl concentrations of [HCl]=1–10 M. As listed in Table 1, the *R* values for the Zr-O shell are 2.20–2.23 Å and the *N* are 6–7. Above 10 M, the coordinated H_2O and/or OH^- are replaced with Cl^- with an increase of [HCl], and the Zr-Cl shell with *R*=2.43 Å appears. This change in the complex structure is reasonably consistent with that of the distribution coefficient (K_d) of Zr on the anion-exchange resin, CA08Y [5]. In the range of 1–7 M, the K_d values of Zr are almost constant, 2–4 mL g^{-1}, while at the higher [HCl], the K_d values increase steeply up to 10^4 mL g^{-1}, forming the anionic hexachloride zirconium, $ZrCl_6^{2-}$, at 11.5 M.

It is also interesting to note that the Zr=O peak with *R*=1.63–1.65 Å is shown in Fig. 1 at 1–5 M, though the Zr=O structure has not been reported in this system. Furthermore, the Zr---Zr peak, which indicates the formation of a dimer complex of Zr, is observed at the lower [HCl] of 1 and 3 M: presumably $[(ZrO)(H_2O)_4]_2(OH)_2$.

Previously, we investigated the anion-exchange behavior of Rf together with Zr and Hf in 4.0–11.5 M HCl [5]. It was found that the adsorption trend of Rf is very similar to that of Zr and Hf, indicating that Rf is typically the member of the group-4 elements. The adsorption order is Rf > Zr > Hf, which reflects a difference in the chloride complexing strength. Recently, we have conducted the EXAFS measurements for Hf in 1.0–11.5 M HCl. In the conference, the Hf result will be compared with that of Zr, and the chloride complexation and hydrolysis of Rf as well as Zr and Hf will be discussed by referring to the ion-exchange and solvent extraction results [1–5].

References

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